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# PATENT SPECIFICATION (11) 1 569 152

(21) Application No. 48294/76 (22) Filed 19 Nov. 1976 (19)
(44) Complete Specification Published 11 Jun. 1980
(51) INT. CL.[3] F23G 7/00
C23G 3/00
F26B 15/00
(52) Index at Acceptance
F4B A13A4A A13C A17 CX
C7E 8

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## (54) USE OF NEUTRALIZING SOLIDS OR GASES IN THE FLUIDIZED BED CLEANING OF CONTAMINATED PIECE PARTS

(71) We, PROCEDYNE CORPORATION of 221 Somerset Street, New Brunswick, New Jersey 08903, United States of America; a corporation organized and existing under the laws of the state of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention relates to a method of clearing a halogen containing plastics coating from a metallic article and to a process of reclaiming piece parts coated or contaminated with halogen containing polymeric materials the processes including the use of a fluidized bed.

So called fluidized solids beds are well known, one field of application being the calibration of thermometers, thermocouples, and other temperature sensing devices, another field of application being the decoating of films on metal substrates by incinerating in a fluidized bed as in U. S. Patent No. 3,250,643. Of more recent interest is the use of a fluidized bed to reclaim useful substrates, usually metallic, contaminated with a substantial quantity of polymer. These situations are accomplished through thermal decomposition of the polymer via pyrolysis and combustion (or incineration) reactions with a predominance of the former to avoid damaging the useful substrate due to over-temperature. This reclamation process is usually referred to as "cleaning of parts" by thermal decomposition.

The phenomenon of fluidized solids is briefly described as follows:

If a vessel containing finely divided inert particles, such as sand, aluminum oxide, and similar refractory materials, is constructed so that a gas (e.g. air, steam, nitrogen) can be passed through the "bed" of particles, a state can be achieved, called "fluidization", in which the individual particles become microscopically separated from eadh other by the moving gas. This "fluidized bed" of particles has unusual properties which differ markedly from those of either the gas or the particles. Instead, the fluidized bed behaves remarkably like a liquid, exhibiting characteristics which are generally attributable to a liquid state. For example, the fluidized bed can be agitated and bubbled and it always seeks a common level. Moreover, various items and parts can be submerged in a fluidized bed in an analogous manner to submerging the item or part in a liquid material. More importantly, if there is a temperature difference between the submerged part and the bed itself, the rate of heat exchange therebetween is relatively rapid.

The most commonly used fluidizing gas is ordinary compressed air obtained from a blower or compressor. For situations where a non-oxidizing atmosphere is required, nitrogen can be utilized and, if a reducing atmosphere is required, steam or cracked gas can be employed with a silicon carbide bed.

The unique characteristic of gas-fluidized solids is the relatively high rate of heat transfer within the phase which yields highly isothermal conditions, as well as excellent heat transfer to solid surfaces submerged in the phase. This characteristic is due to the turbulent motion and rapid circulation rate of the solid particles in conjunction with the extremely high, solid-gas interfacial area. Therefore, despite the fact that gas-solid interfaces normally used have low thermal conductivities, the overall heat transfer characteristics of a fluidized solids phase approach those of a liquid.

This combination of excellent heat transfer characteristic and high heat capacity make fluidized solids an excellent medium for providing an isothermal environment for performing chemical reactions such as pyrolysis, defined as the thermal decomposition of organic materials in the absence of oxygen (typically endothermic), or combustion defined as the

oxidation of materials (typically exothermic) in the presence of oxygen. These reactions are typified by:

pyrolysis

$$\left[\begin{array}{c} \mathrm{H} \\ -\mathrm{C}- \\ \mathrm{H} \end{array}\right]_x \longrightarrow \mathrm{C} + \mathrm{CH_4} + \text{etc.}$$

(endothermic – – heat uptake)

and

combustion

$$\left[\begin{array}{c} \mathrm{H} \\ -\mathrm{C}- \\ \mathrm{H} \end{array}\right]_x + 3/2\,\mathrm{O_2} \longrightarrow \mathrm{CO_2} + \mathrm{H_2O}$$

(exothermic – – heat release)

Of particular interest in this invention is the use of the fluidized bed and the above two reaction mechanisms for the decoating of substrates coated with a polymeric material, as in said Patent No. 3,250,643, or the reclamation of useful substrates contaminated or composited with relatively large quantities of polymeric material such as the reclamation of automobile headrest parts when an imperfect polyurethane cushion has been applied, or the reclamation of the brass in tire valves by decomposition of the rubber composite, i.e. part cleaning by thermal decomposition.

In decoating applications, the predominant reaction is combustion while in reclamation (cleaning) of substrates which are contaminated or part of a composite, the predominant reaction is pyrolysis in order to avoid a high heat release from the high polymer content present, which would otherwise cause damage to the substrate.

In either of these cases, the fluidizing gas is typically air. In many important situations, the polymer being incinerated contains chemical groups which form one or more acidic gases when the polymer is decomposed by incineration and/or pyrolysis. For example, in the reclamation of paint racks or plating racks coated with polyvinylchloride (PVC), typically at 850°F, one of the decomposition products of combustion and/or pyrolysis is gaseous hydrogen chloride. If the reclamation involves some other plastics material containing a halogen (bromine, fluorine, iodine) other than chlorine, the by-product gas will be hydrogen bromide, hydrogen fluoride, or hydrogen iodide (HBr, HF or HI). These and other acid gases or liquids cause the surfaces of the machinery or metal parts being reclaimed to be damaged through corrosion. This, despite the fact that the reclamation operation is carried out at sufficiently low temperatures with predominance of pyrolysis to avoid high temperature regions on the substrate being reclaimed. Thus, the item is rendered useless through corrosion rather than thermal damage.

This situation is typified by the following reactions involving the decomposition of polyvinylchloride type polymers:

incineration

$$[-\mathrm{CH_2} - \underset{\mathrm{Cl}}{\mathrm{CH}}-] + \mathrm{O_2} \longrightarrow \mathrm{CO_2} + \mathrm{HCl} + \mathrm{H_2O}$$

pyrolysis

$$[-\mathrm{CH_2} - \underset{\mathrm{Cl}}{\mathrm{CH}}-] \longrightarrow \mathrm{C} + \mathrm{CH_4} + \mathrm{HCl} + \mathrm{H_2} + \mathrm{C_2H_6}$$

The hydrochloric acid gas leaving the vicinity of the item being reclaimed usually passes the surface of the part, thereby causing corrosive damage. In the case of other types of polymers, the gas may be hydrochloric acid or one or more of the other acid gases.

Typical applications for recovering useful substrates with large organic contamination include the recovery of machine parts such as moulds used in the fabrication of plastic compositions, drawing and extruding dies, metal parts having molded plastic portions such as the recovery of the metal portion of automobile, headrests, dashboards, and bumpers from imperfect or damaged plastic sections and, in general, parts where preservation of dimensions is a primary desideratum. Many of these situations involve polymeric contamination by polymers containing halogens which form acid gases when thermally decomposed.

Accordingly, the present invention seeks to provide a method of cleaning a halogen containing plastics coating from a metallic article and a process of reclaiming piece parts coated or contaminated with halogen containing polymeric materials in which the corrosive gases emitted during the reclamation operation using thermal decomposition are neutralized to prevent damage to the parts being cleaned. More specifically, the present invention seeks to accomplish such neutralization by introducing an alkali metal or alkaline earth metal solid or alkaline gas into the fluidized bed in a form that permits rapid neutralization in the vicinity of the surface of the part being reclaimed.

According to the present invention there is provided a method of cleaning a halogen containing plastics coating from a metallic article by thermally decomposing the plastics coating in such a manner as to prevent the escape into the ambient atmosphere of the halogen gas formed during the decomposition of the coating, said method comprising the steps of:

(a) fluidizing a bed of granular material wherein part or all of the bed comprises at least one reactive carbonate composition selected from the class consisting of alkaline earth metal carbonates, alkali metal carbonates, and combinations thereof;

(b) heating the fluidized bed to a temperature sufficient for complete thermal decomposition of the plastics coating but below the melting point of the metallic article;

(c) fully immersing the plastics coated metallic article within the heated fluidized bed for a time sufficient to complete the thermal decomposition of the plastics coating and allow any halogen gas released by the decomposition to react with the reactive carbonate material of the bed, thereby preventing any halogen containing gas from escaping into the ambient atmosphere; and

(d) removing the cleaned metallic article from the bed.

Also according to the present invention there is provided a process of reclaiming piece parts coated or contaminated with halogen-containing polymeric materials, the reclamation being effected by thermal degradation involving pyrolysis and/or combustion giving rise to the formation of acid gases of the halogen, the piece parts being liable to damage or corrosion if contacted with the acid gases, comprising:

(a) placing the parts in a fluidized bed;

(b) heating or maintaining the bed at a temperature at which the polymeric substances are thermally decomposed by pyrolysis and/or combustion, and

(c) introducing into the bed an alkaline solid material capable of neutralizing the acid gases formed and maintaining a particulate form at the operating temperature of the bed, whereby to prevent the acid gases from damaging or corroding the parts or substrates being cleaned.

In an alternative embodiment, an alkaline gas is introduced into the bed so that the combustion or pyrolysis takes place in the presence of the alkaline gas and the acid gases react with the alkaline gas. The alkaline gas is, in such embodiment, used in place of the alkaline solid material.

The contaminating polymer or other organic material is heated to, or maintained at a temperature sufficient to thermally decompose it by pyrolysis and/or combustion. The presence of the alkali neutralizes the acids almost immediately upon their formation whereby acid corrosion of the metal part is prevented. Limestone may be used as the alkaline solid and, if so, it combines with the acid gas, such as hydrochloric acid gas, according to the following reactions:

$$2HCl + CaCO_3 \longrightarrow CaCl_2 + H_2CO_3$$

and

$$H_2CO_3 \longrightarrow H_2O + CO_2$$

If an alkaline gas is used, such as ammonia, the neutralization of the acid gas, such as hydrochloric acid gas, is typified by the following reaction:

$$HCl + NH_3 \longrightarrow NH_4Cl$$

If a neutralizing solids is used, it should be introduced into the fluidized bed in a sufficiently finely divided form to permit suitable distribution throughout the fluidized bed and with sufficient surface area to maintain a neutralization rate equal to the rate of formation of acid gases. In a typical reclamati n operation at 850°F, it has been found that the neutralizing solids should be subdivided finer than 200 mesh to maintain a sufficiently high neutralization rate.

In the case where an alkaline gas such as ammonia, ($NH_3$) is used, it is desirable, that the gas be introduced in such manner as to prevent its being heated to a sufficiently high temperature to cause decomposition. Since most decoating or reclamation processes take place between 600 - 900°F, there is little decomposition of ammonia to nitrogen and hydrogen as long as the gas is not exposed to any parts of the apparatus which are at a temperature above this.

The invention will be further described, by way of example, with reference to the accompanying drawing, the single Figure of which shows, schematically, an apparatus suitable for carrying out the process of the present invention.

In the drawing, there is shown a vessel 10 having a funnel-shaped bottom 11 defining in part a chamber 10*a* in communication with a pipe 12. Supported in any suitable manner above the chamber 10*a* is a gas-permeable disc 15 which may be porous ceramic material, perforated plate, or other member capable of passing the gas, while supporting the particulate material constituting a fluidized bed 16. The disc must be resistant to breakdown at the operating temperature of the bed.

The bed 16 comprises refractory particles, e.g. sand or aluminium oxide, sized to allow the particles to make intimate contact with the piece part undergoing treatment.

The vessel 10 has a cover 19 which is suitably secured and, together with the bed 16, defines an upper space 21. The bed 16 is heated by any suitable expedient, e.g. a sheathed type of electrical heating element 22 coiled intimately around the vessel 10 and suitably insulated by lagging (not shown). The bed may also be heated radiantly from the outside (not shown).

In order to render the apparatus more versatile, means are provided to feed either air and an alkaline gas, e.g. ammonia, or a gas other than air, e.g. nitrogen, alternatively to the bed. Thus, inlet pipes 12*a*, 12*b* and 12*c* merge into the pipe 12. Each of pipes 12*a*, 12*b* and 12*c* has a conventional flow control valve 25*a*, 25*b*, 25*c* and on-off valves 26*a*, 26*b* and 26*c*. These latter are used to isolate the selected line 12*a*, 12*b* or 12*c* from the unused lines.

Means are provided for supplying steam, water or inert gas to the space 21 to smother the potentially ignitable substances, typically the products of the pyrolysis reactions. This means comprises a supply pipe 41 equipped with a flow meter 42 and a throttling valve 43. The pipe 41 terminates within the space 21 and is capped by a spray nozzle 54 (or other suitable distributor such as multi-point introduction) designed to distribute the smothering medium.

When water is fed through the pipe 41, it is converted into steam in the space 21. When steam or inert gas is fed through pipe 41, less power is required to maintain the fluidized bed at the operating temperature. In either case, water or inert gas is present in the off-gas and dilutes the same to a non-flammable level. The flow of off-gas from the surface of the bed prevents steam or inert gas from entering the bed and contacting the parts being cleaned.

When alkaline solids are used for the neutralization, they comprise part or all of the fluidized solids 16. Since some of the solids are consumed in reaction, it is necessary to periodically add makeup solids to the bed.

When alkaline gas is used, it is continuously added to the fluidizing gas, usually air, through one of the feed lines 12*a* or 12*b*.

As is apparent from the drawing, the piece parts to be cleaned or reclaimed, one of which is shown at *P*, are supported in the bed by any convenient means, e.g. a wire *W*. The part *P* will be intimately subjected to the heated particles of the bed which provide the temperature levels required for the thermal decomposition of the coating or contaminant. When reclaiming substrates from substantial polymer deposits, pyrolysis temperatures typically from 600 - 900°F are employed.

As mentioned, neutralization of acid or acid gas is accomplished by adding an alkaline solid or alkaline gas to the fluidized bed. The solids must be capable of retaining particulate form at the operating temperatures of the fluid bed. In addition, it has been found necessary to use sufficiently finely divided solids to present enough surface area to react with the acid gases formed during thermal decomposition. If the particles are too coarse, the reaction rate of acid formation causes an acid environment in the vicinity of the part being cleaned.

In a typical operation where plating racks coated with polyvinylchloride (PVC) were being reclaimed by this process at a rate of 100 lbs. per hour of PVC on approximately 500 lbs. of metal rack, it was found that a particle size of $CaCO_3$ of less than 200 mesh was required to maintain a neutral environment in the vicinity of the racks.

When using alkaline gas, it must be capable of reacting with the acid formed during thermal decomposition of the polymer and must be stable at bed operating conditions. Ammonia has

been used in a cleaning process involving polyvinylchloride (PVC). It is necessary to ensure that the ammonia is not itself decomposed (cracked) to nitrogen and hydrogen before it is able to react with the acid gases formed. At the temperature involved in cleaning or reclaiming by thermal decomposition where the predominant reaction is pyrolysis, typically 600 - 900°F, the decomposition rate of ammonia is sufficiently low to render it suitable for this neutralization application.

Other potential solids may include hydroxides, oxides, carbonates, and phosphates of alkali metals and alkaline-earth metals. Examples of such solids are calcium oxide (CaO), calcium carbonate ($CaCO_3$), magnesium oxide (MgO), sodium carbonate ($Na_2CO_3$), and potassium hydroxide (KOH), and of alkaline gas, ammonia ($NH_3$) and amines. If desired, the entire bed may consist of particles of an alkali metal or alkaline solid.

In the case of alkaline solids, e.g. calcium carbonate, in the cleaning of polyvinyl chloride, the neutralization reaction is:

$$2HCl + CaCO_3 \longrightarrow CaCl_2 + H_2CO_3$$

$$H_2CO_3 \longrightarrow H_2O + CO_2$$

In the case of an alkaline gas, such as ammonia, introduced into the fluidizing gas stream, the neutralization reaction is:

$$RNH_2 + HCl \longrightarrow RNH_3Cl$$

Where R is hydrogen in ammonia, but may be other alkyl radicals such as methyl ($-CH_3$), ethyl ($-C_2H_5$), methanol ($-CH_2OH$), or ethanol ($-C_2H_4OH$). As *R* becomes a large molecule, these compounds are liquid, but at the elevated temperatures encountered in the fluidized bed cleaning, the amines will be gases. It is important to choose a compound which has a low decomposition reaction rate at the temperature involved.

WHAT WE CLAIM IS:

1. A method of cleaning a halogen containing plastics coating from a metallic article by thermally decomposing the plastics coating in such a manner as to prevent the escape into the ambient atmosphere of the halogen gas formed during the decomposition of the coating, said method comprising the steps of:

(a) fluidizing a bed of granular material wherein part or all of the bed comprises at least one reactive carbonate composition selected from the class consisting of alkaline earth metal carbonates, alkali metal carbonates, and combinations thereof;

(b) heating the fluidized bed to a temperature sufficient for complete thermal decomposition of the plastics coating but below the melting point of the metallic article;

(c) fully immersing the plastics coated metallic article within the heated fluidized bed for a time sufficient to complete the thermal decomposition of the plastics coating and allow any halogen gas released by the decomposition to react with the reactive carbonate material of the bed, thereby preventing any halogen containing gas from escaping into the ambient atmosphere; and

(d) removing the cleaned metallic article from the bed.

2. A process of reclaiming piece parts coated or contaminated with halogen-containing polymeric materials, the reclamation being effected by thermal degradation involving pyrolysis and/or combustion giving rise to the formation of acid gases of the halogen, the piece parts being liable to damage or corrosion if contacted with the acid gases, comprising:

(a) placing the parts in a fluidized bed,

(b) heating or maintaining the bed at a temperature at which the polymeric substances are thermally decomposed by pyrolysis and/or combustion, and

(c) introducing into the bed an alkaline solid material capable of neutralizing the acid gases formed and maintaining a particulate form at the operating temperature of the bed, whereby to prevent the acid gases from damaging or corroding the parts or substrates being cleaned.

3. A process as claimed in Claim 2 wherein the alkaline solid material is selected from the group consisting of alkali metal oxides, alkali metal hydroxides, alkali metal phosphates, alkali metal carbonates, alkaline-earth-metal oxides, alkaline-earth-metal hydroxides, alkaline-earth-metal phosphates and alkaline-earth-metal carbonates.

4. A process as claimed in claim 3 wherein the alkaline solid material is powdered limestone.

5. A process of cleaning or reclaiming piece parts coated or contaminated with halogen-

containing polymeric materials, the reclamation being effected by thermal degradation involving pyrolysis and/or combustion giving rise to the formation of acid gases of the halogen, the piece parts being liable to damage or corrosion if contacted with the acid gases, comprising:

(a) placing the parts in a fluidized bed,

(b) heating or maintaining the bed at a temperature at which the polymeric substances are thermally decomposed by pyrolysis and/or combustion, and

(c) introducing into the bed an alkaline gaseous material capable of neutralizing the acid gases formed, thereby preventing the acid gases from damaging or corroding the parts or substrate being cleaned.

6. A process as claimed in claim 5 wherein the alkaline gas material is ammonia or an amine of the formula $RNH_2$ wherein R is $-CH_3$, $-C_2H_5$, $-CH_2OH$ or $-C_2H_4OH$.

7. A process as claimed in any one of claims 2 to 6 comprising the additional step of introducing water vapor into a space above the fluidized bed to smother ignitable substances resulting from pyrolysis of the contaminating polymer.

8. A process as claimed in any one of claims 2 to 6 comprising the additional step of introducing an inert gas into a space above the fluidized bed to smother ignitable substances resulting from pyrolysis of the contaminating polymer.

9. A method of cleaning a halogen containing plastics coating from a metallic article substantially as hereinbefore described.

10. A process for reclaiming piece parts coated or contaminated with halogen containing polymeric materials substantially as hereinbefore described.

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1980
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained

1569152 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproducti n of the Original on a reduced scale*